

DE 102 37 912 A1 2004.02.26**Sizing of paper, board and cardboard****Abstract****5**

Paper, board and cardboard are engine sized by adding anionic aqueous dispersions of reactive sizes, at least one retention aid and at least one cationic polymer to an aqueous suspension of cellulose fibers and draining the paper stock, and cationic **10** polymers from the group consisting of the polymers containing vinylamine units, polymers containing vinylguanidine units, polyethylenimines, polyamidoamines grafted with ethyleneimine and/or polydiallyldimethylammonium chlorides are used as fixing agents and promoters for anionic aqueous dispersions of a **15** reactive size in the engine sizing of paper, board and cardboard.

20**25****30****35****40****45**

Sizing of paper, board and cardboard

The present invention relates to a process for the engine sizing 5 of paper, board and cardboard by adding aqueous dispersions of anionically dispersed reactive sizes and at least one retention aid to an aqueous suspension of cellulose fibers and draining the paper stock.

10 WO-A-00/23651 discloses aqueous, anionic size dispersions which are obtainable by dispersing a reactive size, such as an alkyldiketene or an alkenylsuccinic anhydride, in the presence of an anionic dispersant in water. Dispersants used are, for example, condensates of naphthalenesulfonic acid and formaldehyde 15 or condensates of phenol, phenolsulfonic acid and formaldehyde or amphiphilic copolymers of hydrophobic monoethylenically unsaturated monomers and hydrophilic monomers having an anionic group. The dispersants may be present in the form of the free acids or of the alkali metal, alkaline earth metal and/or 20 ammonium salts. The size dispersions are added to the paper stock, it being possible, if required, concomitantly to use the drainage aids, flocculants and retention aids and fixing agents conventionally used in papermaking. Retention and distribution of the reactive sizes in the paper are also in need of improvement.

25

It is an object of the present invention to provide an improved process for the sizing of paper, board and cardboard with aqueous dispersions of anionically dispersed reactive sizes in the presence of at least one retention aid, better fixing of the 30 reactive sizes and faster formation of the size being obtained compared with the prior art.

We have found that this object is achieved, according to the invention, by a process for the engine sizing of paper, board and 35 cardboard by adding anionic aqueous dispersions of reactive sizes and at least one retention aid to an aqueous suspension of cellulose fibers and draining the paper stock, if at least one cationic polymer is also added to the aqueous suspension of cellulose fibers.

40

The present invention also relates to the use of cationic polymers from the group consisting of polymers containing vinylamine units, polymers containing vinylguanidine units, polyethyleneimines, polyamidoamines grafted with ethyleneimine 45 and/or polydiallyldimethylammonium chlorides as fixing agents and

promoters for anionic aqueous dispersions of a reactive size in the engine sizing of paper, board and cardboard.

Suitable cellulose fibers are, for example, fibers obtained from 5 mechanical pulp and all annual plants. Mechanical pulp includes, for example, groundwood, thermomechanical pulp (TMP), chemothermomechanical pulp (CTMP), pressure groundwood, semichemical pulp, high-yield pulp and refiner mechanical pulp (RMP) and wastepaper. Chemical pulps, which may be used in 10 bleached or in unbleached form, are also suitable. Examples of these are sulfate, sulfite and soda pulps. Unbleached chemical pulps, which are also referred to as unbleached kraft pulp, are preferably used. Said fibers can be used alone or as a mixture.

15 Suitable engine sizes are, for example, C₁₂- to C₂₂-alkylketene dimers, C₅- to C₂₂-alkyl- or C₅- to C₂₂-alkenylsuccinic anhydrides, C₁₂- to C₃₆-alkyl isocyanates and/or organic isocyanates, such as dodecyl isocyanate, octadecyl isocyanate, tetradecyl isocyanate, hexadecyl isocyanate, eicosyl isocyanate and decyl isocyanate.

20 Preferably used engine sizes are alkylketene dimers and long-chain alkyl- or alkenylsuccinic anhydrides.

Examples of alkylketene dimers are stearyldiketene, lauryldiketene, palmytdiketene, oleyldiketene, behenyldiketene 25 and mixtures thereof. Substituted succinic anhydrides suitable as engine sizes are, for example, decenylsuccinic anhydride, n-octadecenylsuccinic anhydride, dodecenylsuccinic anhydride and n-hexadecenylsuccinic anhydride.

30 The alkyldiketenes and long-chain alkenyl- or alkylsuccinic anhydrides preferred as sizes and processes for the preparation of anionic aqueous dispersions of such reactive sizes are disclosed in WO-A-00/23651 (cf. pages 2 to 12). For the preparation of size dispersions, the reactive sizes are usually 35 heated to a temperature above their melting point and are emulsified in molten form in water under the action of shear forces. The liquid alkenylsuccinic anhydride may be emulsified at as low as room temperature. For example, homogenizers are used for this purpose. The dispersed sizes are stabilized in the 40 aqueous phase using at least one anionic dispersant from the group consisting of the condensates of

(a) naphthalenesulfonic acid and formaldehyde,

45 (b) phenol, phenolsulfonic acid and formaldehyde,

(c) naphthalenesulfonic acid, formaldehyde and urea and

(d) phenol, phenolsulfonic acid, formaldehyde and urea.

5 The anionic dispersants may be present either in the form of the free acids or in the form of the alkali metal, alkaline earth metal and/or ammonium salts. The ammonium salts may be derived both from ammonia and from primary, secondary and tertiary amines, examples of suitable ammonium salts being those of

10 dimethylamine, trimethylamine, hexylamine, cyclohexylamine, dicyclohexylamine, ethanolamine, diethanolamine and triethanolamine. The condensates described above are known and are commercially available. They are prepared by condensation of said components, it also being possible to use corresponding

15 alkali metal, alkaline earth metal or ammonium salts instead of the free acids. Suitable catalysts in the condensation are, for example, acids such as sulfuric acid, p-toluenesulfonic acid and phosphoric acid. Naphthalenesulfonic acid or the alkali metal salts thereof are condensed with formaldehyde, preferably in a

20 molar ratio of from 1 : 0.1 to 1 : 2 and generally in a molar ratio of from 1 : 0.5 to 1 : 1. The molar ratio for the preparation of condensates of phenol, phenolsulfonic acid and formaldehyde is likewise in the abovementioned range, any desired mixtures of phenol and phenolsulfonic acid being used instead of

25 naphthalenesulfonic acid in the condensation with formaldehyde. Instead of phenolsulfonic acid, it is also possible to use the alkali metal and ammonium salts of phenolsulfonic acid. The condensation of the abovementioned starting materials can, if required, additionally be carried out in the presence of urea.

30 For example, from 0.1 to 5 mol of urea are used per mole of naphthalenesulfonic acid or per mole of the mixture of phenol and phenolsulfonic acid.

The condensates have, for example, molar masses of from 800 to

35 100 000, preferably from 1 000 to 30 000, in particular from 4 000 to 25 000. Preferably used anionic dispersants are salts which are obtained, for example, by neutralization of the condensates with lithium hydroxide, sodium hydroxide, potassium hydroxide or ammonia. The pH of the salts is, for example, from 7

40 to 10.

Suitable anionic dispersants are moreover amphiphilic copolymers of

45 (i) hydrophobic monoethylenically unsaturated monomers and

(ii) hydrophilic monomers having an anionic group, such as
monoethylenically unsaturated carboxylic acids,
monoethylenically unsaturated sulfonic acids,
monoethylenically unsaturated phosphonic acids or mixtures
thereof.

Suitable hydrophobic monoethylenically unsaturated monomers

(a) are, for example, olefins of 2 to 150 carbon atoms, styrene,
10 α -methylstyrene, ethylstyrene, 4-methylstyrene,
acrylonitrile, methacrylonitrile, esters of monoethylenically
unsaturated C₃- to C₅-carboxylic acids and monohydric
alcohols, amides of acrylic acid or methacrylic acid with C₁-
to C₂₄-alkylamines, vinyl esters of saturated monocarboxylic
15 acids of 2 to 24 carbon atoms, diesters of maleic acid or
fumaric acid with monohydric C₁- to C₂₄-alcohols, vinyl ethers
of alcohols of 3 to 24 carbon atoms or mixtures of said
compounds.

20 The amphiphilic copolymers contain, as hydrophilic monomers (b),
for example, monoethylenically unsaturated C₃- to C₁₀-carboxylic
acids or anhydrides thereof, 2-acrylamido-2-methylpropanesulfonic
acid, vinylsulfonic acid, styrenesulfonic acid, vinylphosphonic
acid, salts of said monomers or mixtures thereof as hydrophilic
25 monomers having an anionic group

in the form of polymerized units. Particularly preferred are
aqueous size dispersions which contain, as anionic dispersant,
amphiphilic copolymers of

30 (a) α -olefins of 4 to 12 carbon atoms, styrene or mixtures
thereof as hydrophobic monomers and

(b) maleic acid, acrylic acid, methacrylic acid, monoesters of
35 maleic acid and alcohols of 1 to 25 carbon atoms or
alkoxylation products of such alcohols, monoamides of maleic
acid, salts of said monomers or mixtures of these compounds
as hydrophilic monomers having an anionic group

40 in the form of polymerized units and have a molar mass M_w of from
1 500 to 100 000.

Copolymers of maleic anhydride with C₄- to C₁₂-olefins,
particularly preferably C₈-olefins, such as 1-octene and
45 diisobutene, are preferred as anionic dispersants. Diisobutene is
very particularly preferred. The molar ratio of maleic anhydride
to olefin is, for example, from 0.9 : 1 to 3 : 1, preferably from

5

0.95 : 1 to 1.5 : 1. These copolymers are preferably used in a hydrolyzed form as an aqueous solution or dispersion, the anhydride group being present in opened form and preferably some or all of the carboxyl groups being neutralized. The following 5 bases are used for the neutralization: alkali metal bases, such as sodium hydroxide, potassium hydroxide, sodium carbonate or potassium carbonate, alkaline earth metal salts, such as calcium hydroxide, calcium carbonate, magnesium hydroxide, ammonia, primary, secondary or tertiary amines, such as triethylamine, 10 triethanolamine, diethanolamine, ethanolamine, morpholine, etc.

If the amphiphilic copolymers are not sufficiently water-soluble in the form of the free acid, they are used in the form of water-soluble salts, for example the corresponding alkali metal, 15 alkaline earth metal and ammonium salts being used. The molar mass M_w of the amphiphilic copolymers is, for example, from 800 to 250 000, in general from 1 000 to 100 000, preferably from 3 000 to 20 000, in particular from 1 500 to 10 000. The acid numbers of the amphiphilic copolymers are, for example, from 50 to 500, 20 preferably from 150 to 300, mg KOH/g of polymer.

The amphiphilic copolymers are used, for example, in amounts of from 0.05 to 20, preferably from 0.5 to 10, % by weight, based on the reactive size, as an anionic dispersant for the preparation 25 of the size dispersions. The amphiphilic copolymers are preferably used in amounts of from 0.1 to 2, in particular from 0.6 to 1, % by weight, based on the size to be dispersed. With the sole use of amphiphilic copolymers as dispersants, aqueous size dispersions which are formaldehyde-free and have a long 30 shelf life are obtained.

In order to prepare aqueous anionic size dispersions, for example, an aqueous solution or at least one condensate or at least one amphiphilic copolymer may be present and the size 35 dispersed therein at, for example, from 20 to 100°C, preferably from 40 to 90°C. The size is preferably added in the form of a melt and dispersed with vigorous stirring or shearing. The resulting dispersion is cooled in each case. For example, aqueous, anionic size dispersions which contain from 6 to 25% by 40 weight of an alkyldiketene or from 0.1 to 65% by weight of an alkenylsuccinic anhydride dispersed as a size can be prepared in this manner. Highly concentrated size dispersions which contain, for example, from 25 to 60% by weight of an alkyldiketene as a size in the presence of from 0.1 to 5.0% by weight of a 45 condensate of naphthalenesulfonic acid and formaldehyde or at

least one condensate of (b), (c) and/or (d) in dispersed form are preferred.

Further preferred size dispersions contain from 25 to 60% by weight of an alkyldiketene as a size and from 0.1 to 5.0% by weight of an amphiphilic copolymer of

(i) from 95 to 50% by weight of isobutene, diisobutene, styrene or a mixture thereof and

10

(ii) from 5 to 50% by weight of acrylic acid, methacrylic acid, maleic acid, a monoester of maleic acid or a mixture thereof

or of a water-soluble salt of such a copolymer.

15

Such highly concentrated size dispersions have a relatively low viscosity, for example from 20 to 100 mPa.s (measured using a Brookfield viscometer at 20°C). In the preparation of the aqueous dispersions, the pH is, for example, from 2 to 8, preferably from 20 3 to 4. Aqueous, anionic size dispersions having a mean particle size of the sizes of from 0.1 to 3, preferably from 0.5 to 1.5, μm are obtained.

According to the invention, at least one cationic polymer is added as a fixing agent and promoter for reactive sizes, in addition to the abovementioned substances, to the aqueous suspension of cellulose fibers. Examples of cationic polymers are polymers containing vinylamine units, polymers containing vinylguanidine units, polyethyleneimines, polyamidoamines grafted with ethyleneimine and/or polydiallyldimethylammonium chlorides. The amount of cationic polymer is, for example, from 0.001 to 2.0, preferably from 0.01 to 0.1, % by weight, based on dry cellulose fibers.

35 Polymers containing vinylamine units are known, cf. US-A-4,421,602, US-A-5,334,287, EP-A-0 216 387, US-A-5,981,689, WO-A-00/63295 and US-A-6,121,409. They are prepared by hydrolysis of open-chain polymers containing N-vinylcarboxamide units. These polymers are obtainable, for example, by polymerization of 40 N-vinylformamide, N-vinyl-N-methylformamide, N-vinylacetamide, N-vinyl-N-methylacetamide, N-vinyl-N-ethylacetamide and N-vinylpropionamide. Said monomers can be polymerized either alone or together with other monomers.

45 Suitable monoethylenically unsaturated monomers which are copolymerized with the N-vinylcarboxamides are all compounds copolymerizable therewith. Examples of these are vinyl esters of

saturated carboxylic acids of 1 to 6 carbon atoms, such as vinyl formate, vinyl acetate, vinyl propionate and vinyl butyrate, and vinyl ethers, such as C₁- to C₆-alkyl vinyl ether, e.g. methyl or ethyl vinyl ether. Further suitable comonomers are esters, amides 5 and nitriles of ethylenically unsaturated C₃- to C₆-carboxylic acids, for example methyl acrylate, methyl methacrylate, ethyl acrylate and ethyl methacrylate, acrylamide and methacrylamide and acrylonitrile and methacrylonitrile.

10 Further suitable carboxylic esters are derived from glycols or polyalkylene glycols, in each case only one OH group being esterified, e.g. hydroxyethyl acrylate, hydroxyethyl methacrylate, hydroxypropyl acrylate, hydroxybutyl acrylate, hydroxypropyl methacrylate, hydroxybutyl methacrylate and acrylic 15 monoesters of polyalkylene glycols having a molar mass of from 500 to 10 000. Further suitable comonomers are esters of ethylenically unsaturated carboxylic acids with amino alcohols, for example dimethylaminoethyl acrylate, dimethylaminoethyl methacrylate, diethylaminoethyl acrylate, diethylaminoethyl 20 methacrylate, dimethylaminopropyl acrylate, dimethylaminopropyl methacrylate, diethylaminopropyl acrylate, dimethylaminobutyl acrylate and diethylaminobutyl acrylate. The basic acrylates can be used in the form of the free bases, of the salts with mineral acids, such as hydrochloric acid, sulfuric acid or nitric acid, 25 of the salts with organic acids, such as formic acid, acetic acid, propionic acid or the sulfonic acids, or in quaternized form. Suitable quaternizing agents are, for example, dimethyl sulfate, diethyl sulfate, methyl chloride, ethyl chloride and benzyl chloride.

30 Further suitable comonomers are amides of ethylenically unsaturated carboxylic acids, such as acrylamide, methacrylamide and N-alkylmono- and diamides of monoethylenically unsaturated carboxylic acids having alkyl radicals of 1 to 6 carbon atoms, 35 e.g. N-methylacrylamide, N,N-dimethylacrylamide, N-methylmethacrylamide, N-ethylacrylamide, N-propylacrylamide and tert-butylacrylamide, and basic (meth)acrylamides, such as dimethylaminoethylacrylamide, dimethylaminoethylmethacrylamide, diethylaminoethylacrylamide, diethylaminoethylmethacrylamide, 40 dimethylaminopropylacrylamide, diethylaminopropylacrylamide, dimethylaminopropylmethacrylamide and diethylaminopropylmethacrylamide.

Other suitable comonomers are N-vinylpyrrolidone, 45 N-vinylcaprolactam, acrylonitrile, methacrylonitrile, N-vinylimidazole and substituted N-vinylimidazoles, e.g. N-vinyl-2-methylimidazole, N-vinyl-4-methylimidazole,

N-vinyl-5-methylimidazole and N-vinyl-2-ethylimidazole, and N-vinylimidazolines, such as N-vinylimidazoline, N-vinyl-2-methylimidazoline and N-vinyl-2-ethylimidazoline. N-Vinylimidazoles and N-vinylimidazolines are used not only in the form of free bases but also in a form neutralized or 5 quaternized with mineral acids or organic acids, the quaternization preferably being carried out with dimethyl sulfate, diethyl sulfate, methyl chloride or benzyl chloride. Diallyldialkylammonium halides, e.g. diallyldimethylammonium 10 chloride, are also suitable.

The copolymers contain, for example,

- from 95 to 5, preferably from 90 to 10, mol% of at least one 15 N-vinylcarboxamide and

- from 5 to 95, preferably from 10 to 90, mol% of other monoethylenically unsaturated monomers copolymerizable therewith

20 in the form of polymerized units. The comonomers are preferably free of acid groups.

In order to prepare polymers containing vinylamine units, it is 25 preferable to start from homopolymers of N-vinylformamide or from copolymers which are obtainable by copolymerization of

- N-vinylformamide with
30 - vinyl formate, vinyl acetate, vinyl propionate, acrylonitrile, N-vinylcaprolactam, N-vinylurea, N-vinylpyrrolidone or C₁- to C₆-alkyl vinyl ethers

and subsequent hydrolysis of the homopolymers or of the 35 copolymers with formation of vinylamine units from the polymerized N-vinylformamide units, the degree of hydrolysis being, for example, from 5 to 100, preferably from 70 to 100, mol%. The hydrolysis of the polymers described above is effected by the action of acids, bases or enzymes by known methods. When 40 acids are used as the hydrolyzing agent, the vinylamine units of the polymers are present as ammonium salt, whereas the free amino groups form in the case of hydrolysis with bases.

In most cases, the degree of hydrolysis of the homo- and 45 copolymers is from 80 to 95 mol%. The degree of hydrolysis of the homopolymers is equivalent to the content of vinylamine units in the polymers. In the case of copolymers which contain vinyl

esters as polymerized units, hydrolysis of the ester groups with formation of vinyl alcohol units may occur in addition to the hydrolysis of the N-vinylformamide units. This is the case in particular when the hydrolysis of the copolymers is carried out 5 in the presence of sodium hydroxide solution. Acrylonitrile in the form of polymerized units is likewise chemically modified during the hydrolysis. Here, for example, amido groups or carboxyl groups form. The homo- and copolymers containing vinylamine units can, if required, contain up to 20 mol% of 10 amidine units, which form, for example, by reaction of formic acid with two neighboring amino groups or by intramolecular reaction of an amino group with a neighboring amido group, for example of N-vinylformamide in the form of polymerized units. The molar masses M_w of the polymers containing vinylamine units are, 15 for example, from 500 to 10 million, preferably from 1 000 to 5 million (determined by light scattering). This molar mass range corresponds, for example, to K values of from 5 to 300, preferably from 10 to 250 (determined according to H. Fikentscher in 5% strength aqueous sodium chloride solution at 25°C and a 20 polymer concentration of 0.5% by weight). Cationic polymers which have K values of from 50 to 135 are particularly preferably used.

The polymers containing vinylamine units are preferably used in salt-free form. Salt-free aqueous solutions of polymers 25 containing vinylamine units can be prepared, for example, from the salt-containing polymer solutions described above with the aid of ultrafiltration of suitable membranes at cut-offs of, for example, from 1 000 to 500 000, preferably from 10 000 to 300 000, Dalton. Furthermore, the aqueous solutions of other 30 polymers containing amino and/or ammonium groups, which solutions are described below, can be obtained in salt-free form with the aid of ultrafiltration.

Derivatives of polymers containing vinylamine units may also be 35 used as cationic polymers. For example, it is possible to prepare a multiplicity of suitable derivatives from the polymers containing vinylamine units, by amidation, alkylation, sulfonamide formation, urea formation, thiourea formation, carbamate formation, acylation, carboxymethylation, 40 phosphonomethylation or Michael addition of the amino groups of the polymer. Of particular interest here are uncrosslinked polyvinylguanidines, which are obtainable by reaction of polymers containing vinylamine units, preferably polyvinylamines, with cyanamide (R^1R^2N-CN , where R^1 and R^2 are each H, C_1 - to C_4 -alkyl, 45 C_3 - to C_6 -cycloalkyl, phenyl, benzyl, alkyl-substituted phenyl or

naphthyl), cf. US-A-6,087,448, column 3, line 64 to column 5, line 14.

The polymers containing vinylamine units also include hydrolyzed 5 graft polymers of, for example, N-vinylformamide on polyalkylene glycols, polyvinyl acetate, polyvinyl alcohol, polyvinylformamides, polysaccharides, such as starch, oligosaccharides or monosaccharides. The graft polymers are obtainable by subjecting, for example, N-vinylformamide to free 10 radical polymerization in an aqueous medium in the presence of at least one of said grafting bases, if required together with other copolymerizable monomers, and then hydrolyzing the grafted-on vinylformamide units in a known manner to give vinylamine units.

15 Further suitable cationic polymers are polyethyleneimines, which can be prepared, for example, by polymerization of ethyleneimine in aqueous solution in the presence of acid-eliminating compounds, acids or Lewis acids as a catalyst. Polyethyleneimines have, for example, molar masses of up to 2 million, preferably 20 from 200 to 1 000 000. Polyethyleneimines having molar masses of from 500 to 750 000 are particularly preferably used. The polyethyleneimines can, if required, be modified, for example alkoxylated, alkylated or amidated. They can moreover be subjected to a Michael addition or a Stecker synthesis. The 25 polyethyleneimine derivatives obtainable thereby are likewise suitable as cationic polymers.

Polyamidoamines grafted with ethyleneimine and obtainable, for example, by condensation of dicarboxylic acids with polyamines 30 and subsequent grafting on of ethyleneimine are also suitable. Suitable polyamidoamines are obtained, for example, by reacting dicarboxylic acids of 4 to 10 carbon atoms with polyalkylenepolyamines which contain from 3 to 10 basic nitrogen atoms in the molecule. Examples of dicarboxylic acids are 35 succinic acid, maleic acid, adipic acid, glutaric acid, suberic acid, sebacic acid and terephthalic acid. In the preparation of the polyamidoamines, it is also possible to use mixtures of dicarboxylic acids, as well as mixtures of a plurality of polyalkylenepolyamines. Suitable polyalkylenepolyamines are, for 40 example, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, dipropylenetriamine, tripropylenetetramine, dihexamethylenetriamine, aminopropylethylenediamine and bisaminopropylethylenediamine. For the preparation of the polyamidoamines, the dicarboxylic acids 45 and polyalkylenepolyamines are heated to relatively high temperatures, for example to temperatures in the range from 120 to 220°C, preferably from 130 to 180°C. The water formed during

11

the condensation is removed from the system. During the condensation, lactones or lactams of carboxylic acids of 4 to 8 carbon atoms can, if required, also be used. For example, from 0.8 to 1.4 mol of a polyalkylenepolyamine are used per mole of a 5 dicarboxylic acid. These polyamidoamines are grafted with ethyleneimine. The grafting reaction is carried out, for example, in the presence of acids or Lewis acids, such as sulfuric acid or boron trifluoride etherates, at, for example, from 80 to 100°C. Compounds of this type are described, for example, in

10 DE-B-24 34 816.

The uncrosslinked or crosslinked polyamidoamines, which, if required, are additionally grafted with ethyleneimine before the crosslinking, are also suitable as cationic polymers. The 15 crosslinked polyamidoamines grafted with ethyleneimine are water-soluble and have, for example, an average molecular weight M_w of from 3 000 to 2 million Dalton. Conventional crosslinking agents are, for example, epichlorohydrin or bischlorohydrin ethers of alkylene glycols and polyalkylene glycols.

20

Other suitable cationic polymers are polyallylamines. Polymers of this type are obtained by homopolymerization of allylamine, preferably in a form neutralized with acids, or by copolymerization of allylamine with other monoethylenically 25 unsaturated monomers which are described above as comonomers for N-vinylcarboxamides.

Water-soluble crosslinked polyethyleneimines which are obtainable by reaction of polyethyleneimines with crosslinking agents, such 30 as epichlorohydrin or bischlorohydrin ethers of polyalkylene glycols having from 2 to 100 ethylene oxide and/or propylene oxide units, and still have free primary and/or secondary amino groups are also suitable. Amidic polyethyleneimines which are obtainable, for example, by amidation of polyethyleneimines with 35 C_1 - to C_{22} -monocarboxylic acids are also suitable. Further suitable cationic polymers are alkylated polyethyleneimines and alkoxyated polyethyleneimines. In the alkoxylation, for example, from 1 to 5 ethylene oxide or propylene oxide units are used per NH unit in the polyethyleneimine.

40

The abovementioned cationic polymers have, for example, K values of from 8 to 300, preferably from 50 to 135 (determined according to H. Fikentscher in 5% strength aqueous sodium chloride solution at 25°C and a polymer concentration of 0.5% by weight). At a pH of 45 4.5, they have, for example, a charge density of at least 1, preferably at least 4, meq/g of polyelectrolyte.

12

Preferred cationic polymers are polymers containing vinylamine units and polyethyleneimines. Examples of these are:

v vinylamine homopolymers, from 10 to 100% hydrolyzed

5 polyvinylformamides, partially or completely, preferably 85 – 95%, hydrolyzed copolymers of vinylformamide and vinyl acetate, vinyl alcohol, vinylpyrrolidone or acrylamide, in each case having K values of from 50 to 135, in particular from 80 to 95, and

10

polyethyleneimines, crosslinked polyethyleneimines or amidated polyethyleneimines, which in each case have molar masses of from 500 to 3 000 000.

The polymer content of the aqueous solution is, for example, from

15 1 to 60, preferably from 2 to 15, in general from 5 to 10, % by weight.

The production of paper, board and cardboard is usually effected by draining a suspension of cellulose fibers. The use of kraft

20 pulp is particularly preferred. The use of TMP and CTMP is furthermore of particular interest. The pH of the cellulose fiber suspension is, for example, from 4 to 8, preferably from 6 to 8. The paper stock can be drained batchwise or continuously on a paper machine. The sequence of the addition of cationic polymer,

25 engine size and retention aid can be freely chosen. However, the procedure in which first the cationic polymer, preferably polyvinylamine, and then at least one reactive size, such as an alkylketene dimer, alkyl- or alkenylsuccinic anhydride or a mixture of the engine sizes, are added to the aqueous cellulose

30 fiber suspension is preferred. At least one retention aid is then metered in. According to another embodiment of the novel process, first at least one engine size, then the retention aid and finally the cationic polymer are metered in.

35 After draining of the paper stock and drying of the paper product, engine-sized paper products, such as paper, board or cardboard having a basis weight of from 20 to 400, preferably from 40 to 200, g/m², are obtained.

40 When alkyldiketene dispersions are used as sizes for paper, the full sizing effect is known to develop only after prolonged storage of the sized papers. Surprisingly, the polymers to be used according to the invention and containing vinylamine units act as promoters in the sizing of paper with aqueous, anionic

45 alkyldiketene dispersions. When combinations of aqueous, anionic alkyldiketene dispersions and polyvinylamines are used as engine sizes for paper, rapid formation of the size is obtained, so that

13

the paper sized with this combination can be further processed immediately after their production, for example they can be coated with paper coating slips or printed on without prolonged storage.

5

The draining of the paper stock is additionally effected in the presence of a retention aid. Apart from anionic retention aids or nonionic retention aids, such as polyacrylamides, cationic polymers are preferably used as retention aids and as drainage

10 aids. This results in a significant improvement in the runnability of the paper machines. Cationic retention aids which may be used are all products commercially available for this purpose. These are, for example, cationic polyacrylamides,

polydiallyldimethylammonium chlorides, high molecular weight

15 polyvinylamines, polyethyleneimines, polyamines having a molar mass of more than 50 000, modified polyamines which are grafted with ethyleneimine and, if required, crosslinked, polyetheramides, polyvinylimidazoles, polyvinylpyrrolidines, polyvinylimidazolines, polyvinyltetrahydropyrines,

20 poly(dialkylaminoalkyl vinyl ethers), poly(dialkylaminoalkyl (meth)acrylates) in protonated or in quaternized form and polyamidoamines obtained from a dicarboxylic acid, such as adipic acid, and polyalkylenepolyamines, such as diethylenetriamine, which are grafted with ethyleneimine and crosslinked with

25 polyethylene glycol dichlorohydrin ethers according to DE-B-24 34 816, or polyamidoamines which have been reacted with epichlorohydrin to give water-soluble condensates, and copolymers of acrylamide or methacrylamide and dialkylaminoethyl acrylates or methacrylates, for example copolymers of acrylamide and

30 dimethylaminoethyl acrylate in the form of the salt with hydrochloric acid or in the form quaternized with methyl chloride. Further suitable retention aids are microparticle systems comprising cationic polymers, such as cationic starch, and finely divided silica, or comprising cationic polymers, such

35 as cationic polyacrylamide, and bentonite.

The cationic polymers which are used as retention aids have, for example, Fikentscher K values of at least 140 (determined in 5% strength aqueous sodium chloride solution at a polymer

40 concentration of 0.5% by weight, a temperature of 25°C and a pH of 7). They are preferably used in amounts of from 0.01 to 0.3% by weight, based on dry cellulose fibers.

Unless evident otherwise from the context, the stated percentages

45 in the examples are by weight. The K values were determined according to H. Fikentscher, Cellulose-Chemie (1932), 13, 58-64 and 71-74, in 5% strength aqueous sodium chloride solution at 25°C

14

and a pH of 7 at a polymer concentration of 0.5% by weight. The molar masses Mw of the polymers were measured by light scattering.

5 Examples

Ink flotation time

10 The ink flotation time (measured in minutes) is the time which a test ink according to DIN 53126 requires for 50% strike-through through a test sheet.

Cobb value

15 This was determined according to DIN 53 132 by storage of the paper sheets for a period of 60 seconds in water. The water absorption is stated in g/m².

Polyvinylamine A

20 Cationic polymer which was obtained by hydrolysis of poly-N-vinylformamide having a K value of 90 with a degree of hydrolysis of 95 mol% (polymer which contained 95 mol% of vinylamine units and 5 mol% of vinylformamide units).

25 Anionic engine size A

30 Aqueous dispersion of a mixture of palmityldiketene and stearyldiketene, prepared according to example 1 of WO-A-00/23651 with the sodium salt of the condensate of naphthalenesulfonic acid with formaldehyde in a molar ratio of 1 : 0.8 and having a molar mass Mw of 7 000 as an anionic dispersant.

Example 1

35 0.08% of the anionic engine size A, 0.04% of commercial cationic polyacrylamide (Polymin® KE 2020) and 0.1% of polyvinylamine A, based in each case on dry cellulose fiber mixture, were added to a paper stock having a consistency of 8 g/l and comprising a 40 completely bleached mixture of 70% of pine sulfate pulp and 30% of birch sulfate pulp, having a freeness of 35° (Schopper-Riegler). The pH of the mixture was brought to 7.0. The mixture was then processed on a Rapid-Köthen sheet former to give a sheet having a basis weight of 100 g/m². The sheet was then 45 dried on a steam-heated drying cylinder at 90°C to a water content of 6%. After the drying, the Cobb value and the ink flotation

15

time of the sheet were determined. The results are shown in the table.

Example 2

5

Example 1 was repeated with the single exception that the amount of polyvinylamine A was increased to 0.2%. The results obtained are shown in the table.

10 Example 3

Example 1 was repeated with the single exception that the amount of polyvinylamine A was increased to 0.6%. The results obtained are shown in the table.

15

Comparative example 1

0.08% of a commercial aqueous dispersion stabilized with cationic starch and comprising an alkyldiketene dimer (Basoplast® 2030 LC)

20 and 0.04% of a cationic polyacrylamide (Polymin® KE 2020), based in each case on dry cellulose fiber mixture, were added to a paper stock having a consistency of 8 g/l and comprising a completely bleached mixture of 70% of pine sulfate pulp and 30% of birch sulfate pulp, having a freeness of 35°

25 (Schopper-Riegler). The pH of the mixture was brought to 7.0. The mixture was then processed on a Rapid-Köthen sheet former to give a sheet having a basis weight of 100 g/m². The sheet was then dried on a steam-heated drying cylinder at 90°C to a water content of 6%. After the drying, the Cobb value and the ink flotation

30 time of the sheet were determined. The results are shown in the table.

Comparative example 2

35 Comparative example 1 was repeated with the single exception that, after the metering of Polymin® KE 2020, commercial cationic starch (Solvitose®BKN) was added in an amount of 0.6%. The results obtained are shown in the table.

40 Comparative example 3

Comparative example 1 was repeated with the single exception that, after the metering of Polymin®KE 2020, polyvinylamine A was metered in an amount of 0.2% to the paper stock. The results are

45 shown in the table.

16

Table

	Example	Cobb value (60 seconds) [g/m ²]	Ink flotation time [sec]
5	1	30	24
	2	27	26
	3	25	60
Comparative example			
10	1	26	25
	2	25	35
	3	27	26

15**20****25****30****35****40****45**

We claim:-

1. A process for the engine sizing of paper, board and cardboard
5 by adding anionic aqueous dispersions of reactive sizes and at least one retention aid to an aqueous suspension of cellulose fibers and draining the paper stock, wherein at least one cationic polymer is also added to the aqueous suspension of cellulose fibers.
- 10 2. A process as claimed in claim 1, wherein the cationic polymers used are polymers containing vinylamine units, polymers containing vinylguanidine units, polyethyleneimines, polyamidoamines grafted with ethyleneimine and/or polydiallyldimethylammonium chlorides.
- 15 3. A process as claimed in claim 1 or 2, wherein the cationic polymers used are polymers containing vinylamine units and/or polyethyleneimines.
- 20 4. A process as claimed in any of claims 1 to 3, wherein the cationic polymers used are from 10 to 100 mol% hydrolyzed homo- or copolymers of N-vinylformamide.
- 25 5. A process as claimed in any of claims 1 to 4, wherein the cationic polymers used are polyvinylamines.
6. A process as claimed in any of claims 1 to 5, wherein the sizes used are C₁₂- to C₂₀-alkylketene dimers, C₅- to C₂₂-alkyl or C₅- to C₂₂-alkenylsuccinic anhydrides and/or C₁₂- to C₃₆-alkyl isocyanates.
- 30 7. A process as claimed in any of claims 1 to 6, wherein C₁₄- to C₁₈-alkylketene dimers are used together with polymers containing vinylamine units.
- 35 8. A process as claimed in any of claims 1 to 7, wherein first at least one cationic polymer and then the anionic aqueous dispersion of a reactive size are metered into the aqueous suspension of cellulose fibers.
- 40

18

9. A process as claimed in any of claims 1 to 7, wherein first an anionic aqueous dispersion of a reactive size is metered into the aqueous suspension of cellulose fibers and then a cationic polymer.

5

10. The use of cationic polymers from the group consisting of the polymers containing vinylamine units, polymers containing vinylguanidine units, polyethyleneimines, polyamidoamines grafted with ethyleneimine and/or polydiallyldimethylammonium chloride as fixing agents and promoters for anionic aqueous dispersions of a reactive size in the engine sizing of paper, board and cardboard.

15

20

25

30

35

40

45